Alternates to Chromates

1. Product Sustainability Tracking by UTC: Materials of Concern
2. Progress in Chromate Elimination from Aerospace Applications
3. Barriers to Complete Chromate Elimination

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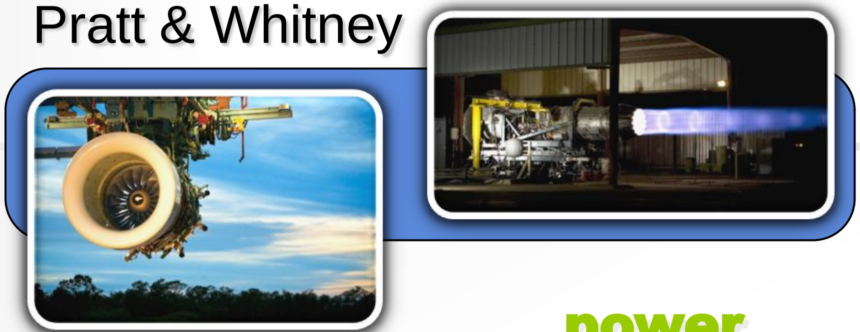
United Technologies Research Center

United Technologies

Business units

aerospace systems

Pratt & Whitney



Sikorsky

Hamilton Sundstrand

power solutions

UTC Power

building systems

Carrier

UTC Fire & Security

Otis

Tracking and Reporting Materials of Concern

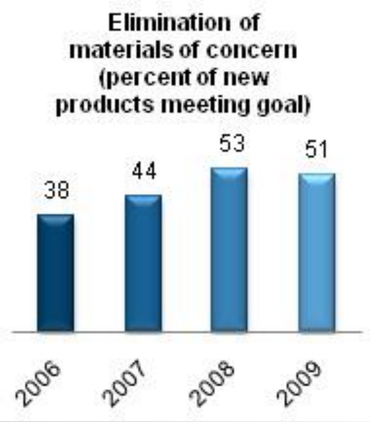
Materials of Concern

Heavy Metals

	Chemical Name
	Cadmium & Compounds
	Hexavalent Chromium (compounds and solutions)
	Lead & Compounds
	Mercury & Compounds

Chlorinated Solvents

CAS#	Chemical Name
00075-09-2	Dichloromethane (methylene chloride)
00127-18-4	Tetrachloroethylene (perchloroethylene)
00071-55-6	1,1,1 - trichloroethylene
00079-01-6	Trichloroethylene
00067-66-3	Trichloromethane



2009 Annual Report

UTC has a portfolio of products and services that deliver significant energy savings to our customers. Our fuel cells have been in use for nearly 50 years and today power everything from supermarkets to space shuttles. We also manufacture combined heat and power systems. Our geothermal products tap previously unusable geothermal reserves for renewable and continuously available power.

In 2009, UTC participated in working groups with the World Resources Institute and the World Business Council for Sustainable Development to draft the Product Life Cycle Accounting and Reporting Standard for Greenhouse Gases.

2009 Progress

Improve the energy efficiency and reduce packaging of new products by 10 percent. New UTC products released in 2009 improved in energy efficiency by an average of 25 percent. New products introduced included several Carrier chillers, new models of Otis' Gen2 elevators and the FlexiFOG micro water-mist fire suppression system from UTC Fire & Security. New product packaging was reduced by 23 percent, driven primarily by the redesign of packaging for Carrier and Otis products.

Continue to eliminate materials of concern in the manufacture and maintenance of all new products. UTC achieved a 51 percent reduction in new products released in 2009. This is down slightly from the 53 percent reduction in new products released in 2008.

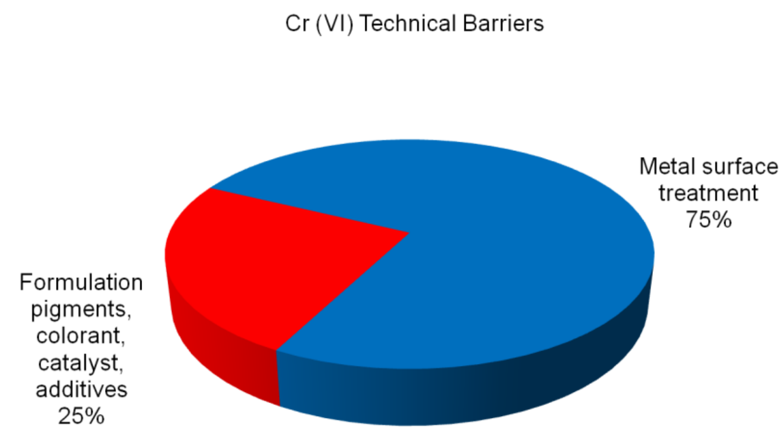
2010 Objectives

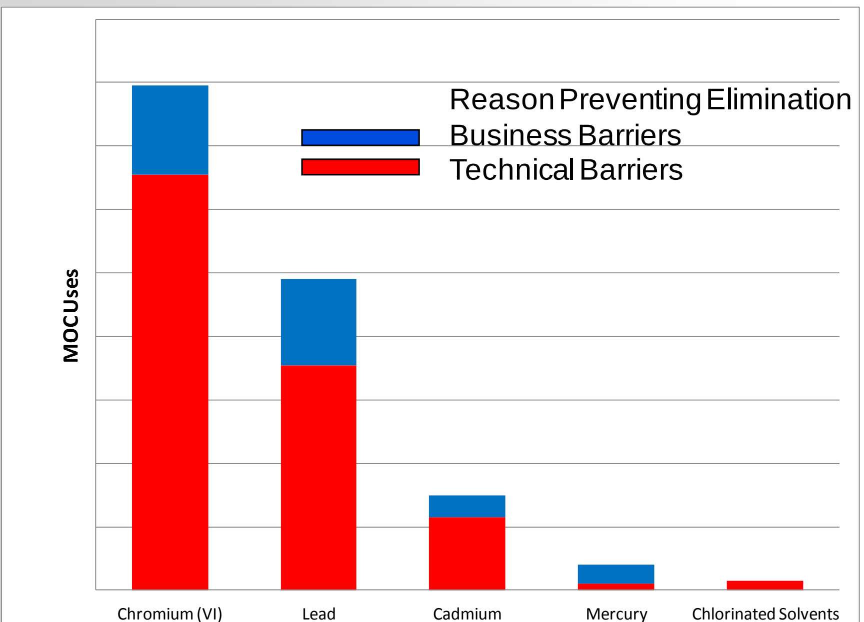
- **Improve energy efficiency and reduce new product packaging by 10 percent through 2010.**
- **Work to eliminate materials of concern.**

Chromate surface treatments dominate MOC use in new products

Three High Risk Barriers Identified:

1. Robust anticorrosion conversion coatings for 2000-series Al
2. Non chromate treatments for surface conductivity preservation
3. Non chromate adhesive bond primers





	Anodizing	Conv. Coating	Priming
High Risk		1. Stable surface conductivity 2. Corrosion protection of 2000-series Al	1. Corrosion resistance of adhesive primers
Moderate	1. Entrapment 2. Hardcoat masking 3. BSAA 2000-series Al 4. Optimal sealing 5. Supplier readiness	1. Common TCP spec 2. Process optimization	1. Paint primer use on interiors

Chromate Replacement Success at Sikorsky Aircraft

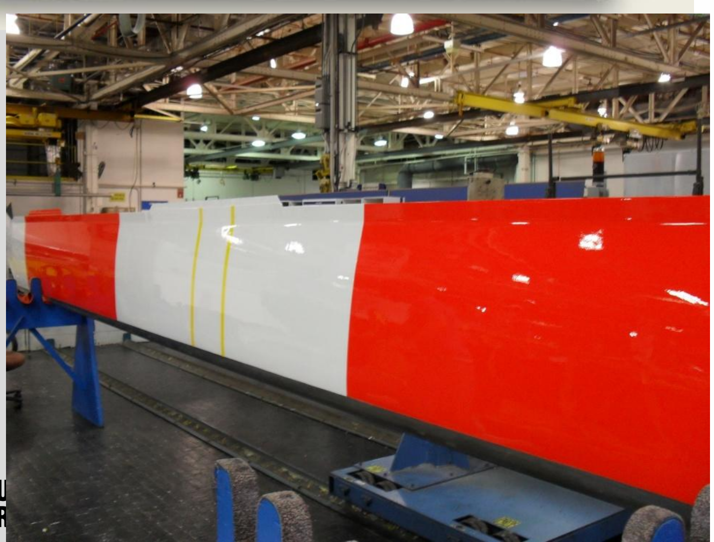
Military Applications

First military aircraft applied with non-chrome paint primer

2008

First military rotor blade applied with non-chrome primer

2010



Commercial Blade Coating System

- Non-chromated paint system
- Lead the Fleet evaluation in process - 2010
- Basecoat/Clear coat system
- Less reworks
- Buffable
- Eliminates sanding surfacer step

P&W Progress in Cr+6 Elimination

Pratt & Whitney
A United Technologies Company

Chromate-free Paint Primer

- ✓ Cr-free paint primer approved for 6000 series AA
- ❖ Elimination of hexavalent Cr paint primer on Geared Turbofan™ engine

Chromate-free anodizing

- ✓ AMS 2471 & BSAA approved for production use
- ❖ Elimination of AMS 2470 for P&W designs on Geared Turbofan™ engine

Chromate-free anodize sealing and conversion coating

- ✓ Trivalent Cr sealing approved for AMS 2471 sulfuric acid anodizing
- ✓ Trivalent Cr sealing of BSAA undergoing final validation testing
- ✓ Trivalent Cr sealing approved for AMS 2417 ZnNi plating
- ❖ Elimination of hexavalent Cr seal for P&W designs on Geared Turbofan™ engine

- ✓ Trivalent Cr approved for conversion coating touchup of 6061 Al

P&W-developed trivalent Cr conversion coating / anodize seal chemistry is available commercially

- ✓ Chemistry includes an adhesion promoting additive
- ✓ Available as Metalast TCP-NP, SurTec 648TCRP

1. Robust anticorrosion conversion coatings for 2000-series Al

- Chromate conversion coatings are used in thousands of UTC components, including new designs
- They provide corrosion inhibition and stable surface conductivity for electrical connections
- Extensive UTRC/UTC / Industry / DoD testing over 20 years has identified a single promising alternative – ZrO_2/Cr^{+3} conversion coatings (TCP)

- **These coatings are not robust enough for protection of 2000-series Al alloys to widely implement in aerospace applications**
  - Accelerated Corrosion Life - too short: 400 h vs 1000+ h for chromate coatings
  - “Infant Mortality” – too high: 18% vs 10% for chromate coatings

2024-T3 Al, TCP treatment, 1656 hrs Neutral Salt Spray

2024-T3 Al, no treatment, 408 hrs Neutral Salt Spray

Simplified Reaction Scheme for TCP Film Formation

Hydrolysis of Chromium Sulfate:
$Cr_2(SO_4)_3 + 6H_2O \rightarrow 2Cr(OH)_3 + 3\ H_2SO_4$
pH, [$SO_4$2-]

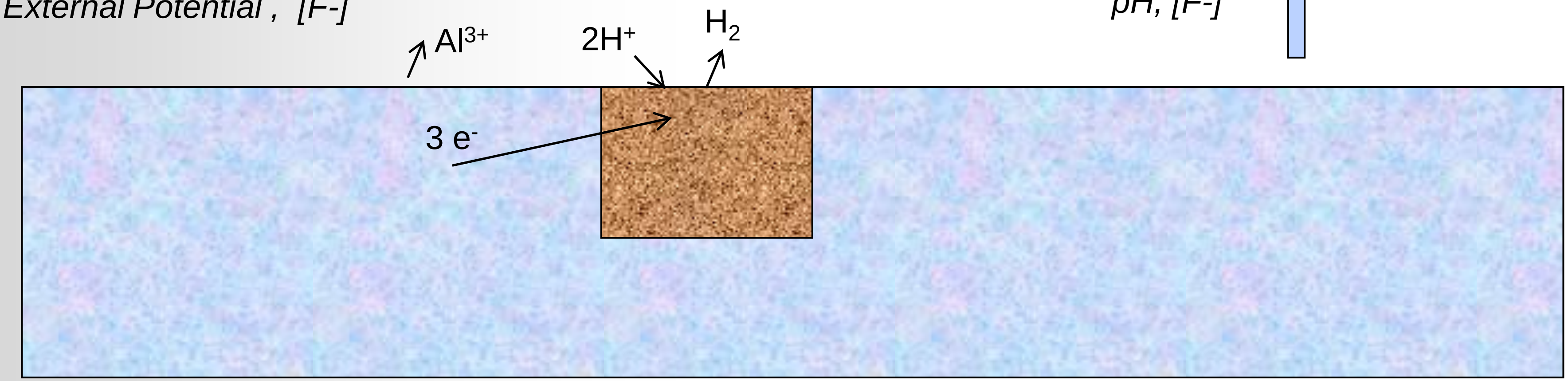
Hydrolysis of Potassium Fluoriziconate :
$K_2ZrF_6 + 6H_2O \rightarrow Zr(OH)_4 + 6HF + 2\ KOH$
pH, [F-]

Fluoride Complexation of Aluminum:
$AlF_3 \rightarrow AlF_4^- \rightarrow AlF_5^{2-} \rightarrow AlF_6^{3-}$
pH, [F-]

Dissolution of Aluminum:
$2Al + 6\ HF \rightarrow 2\ AlF_3 + 3H_2$
External Potential , [F-]

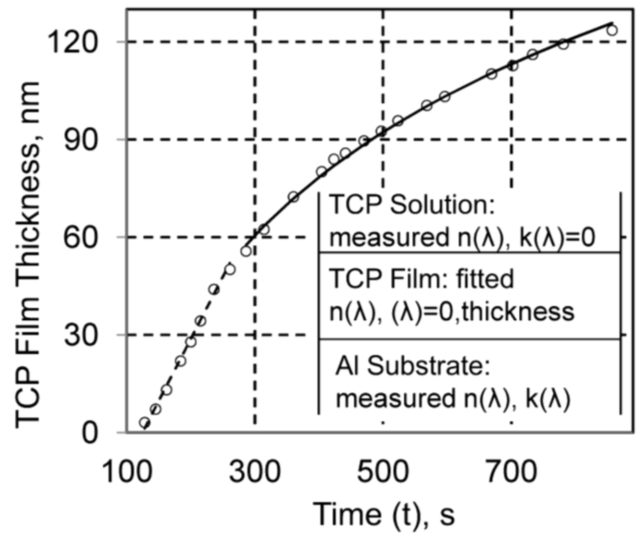
Hydrogen Evolution
External Potential

Dissolution of Aluminum Oxide:
$Al_2O_3 + 6HF \rightarrow 2\ AlF_3 + 6H_2O$
pH, [F-]



Formation Mechanism of TCP Films – General Observations

In situ Spectroscopic Ellipsometry Studies of Trivalent Chromium Coating on Aluminum”, Applied Physics letters, in press

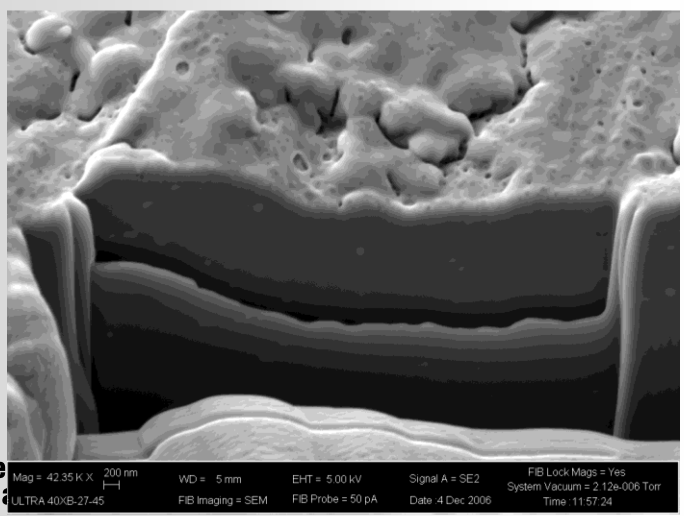


•In-situ monitoring reveals:

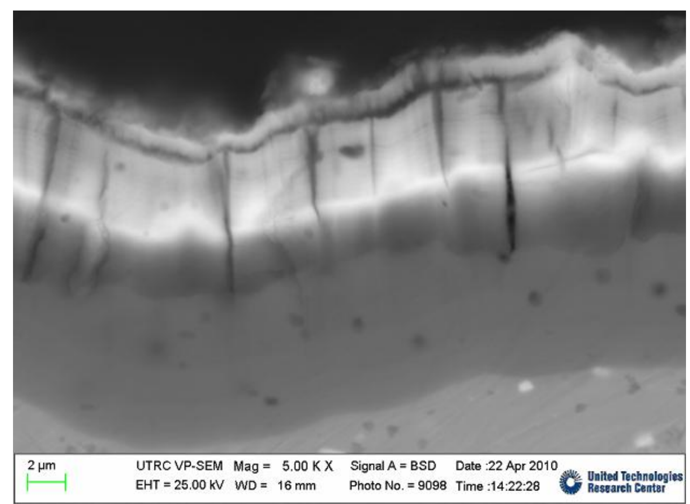
1. Activation phase (0-120 s)
   - Dissolution of native oxide
2. Film growth initiation (120-300 s)
3. Consolidation phase (300+ s)
   - Suspected hydrolysis and crystallization within the film

- Deposition reaction is likely non-Faradaic
  - 100X higher deposition rate on anodized Al (dielectric surface layer)

50 nm TCP film on Bare 2024 Al – 10 minute deposition time



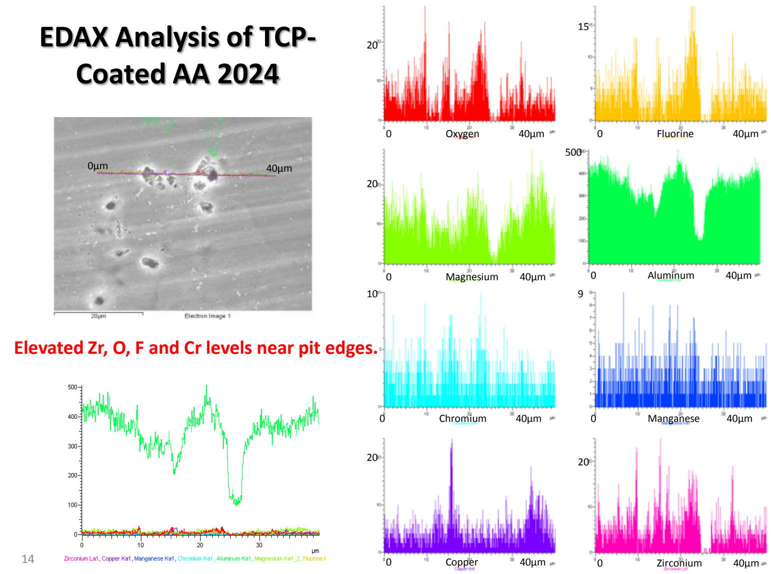
5 um TCP film on anodized Al – 10 minute deposition time



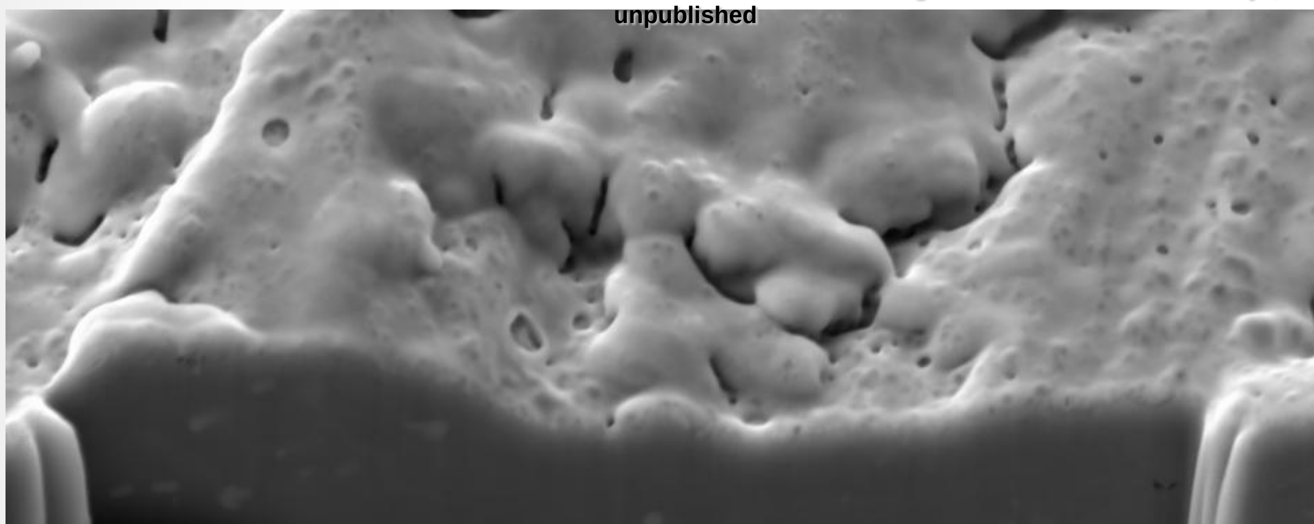
Formation Mechanism of TCP Films- Local Effects

- Surface analysis by SERDP team partners shows local enrichment of TCP-film elements in the vicinity of exposed intermetallic particles on the surface

- FIB / SEM imaging by UTRC reveals structural defects in TCP films , similar in size and shape to intermetallic particles



Source: Greg Swain, MSU, **Structure, Function and Stability of Trichrome Process Coatings Formed on Aluminum Alloys, unpublished**



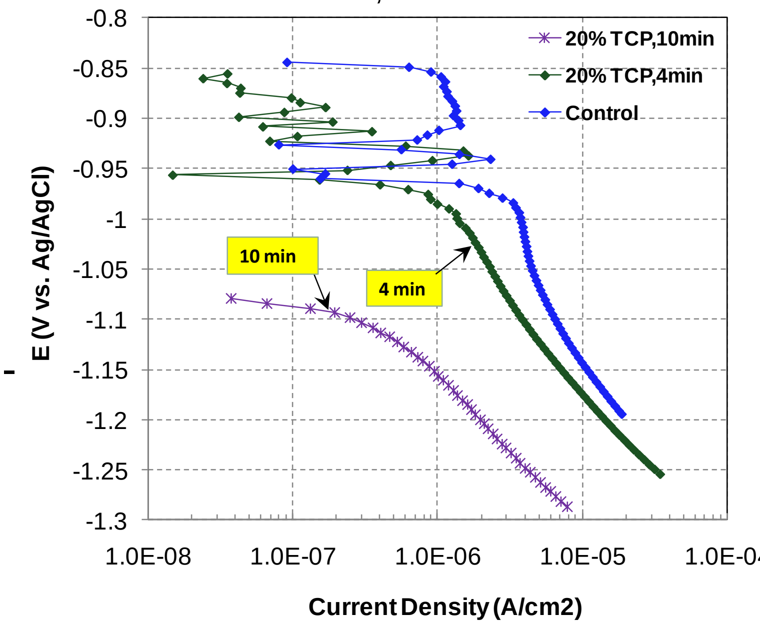
Protection Mechanisms for TCP Films

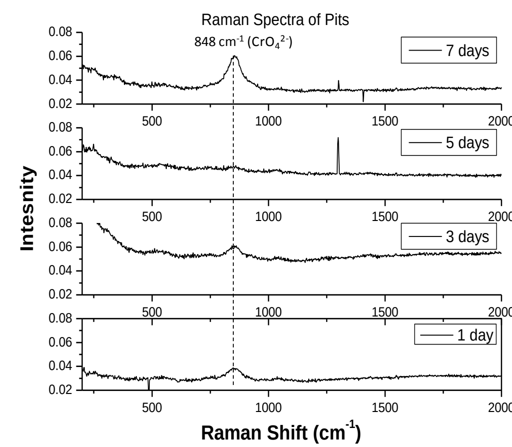
- UTRC measurements indicate that TCP coatings provide cathodic corrosion inhibition
  - Suppression of the oxygen reduction reaction
  - Cathodic reactions known to be localized to intermetallic particles

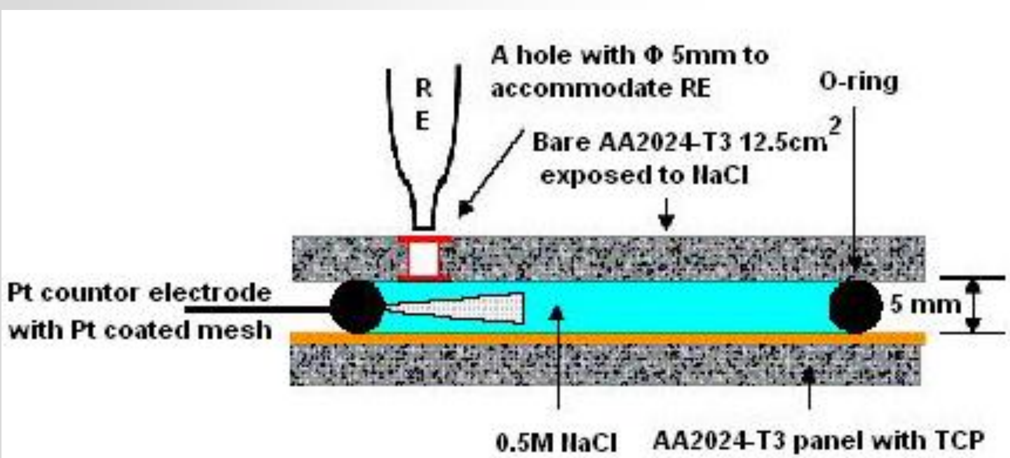
- OSU measurements show transference of Cr from TCP-treated to bare 2024 in an “artificial scratch” cell

- Raman spectroscopy by MSU indicates highly localized formation of Cr+6 compounds under corrosive stress conditions

Source: Lei Chen, UTRC







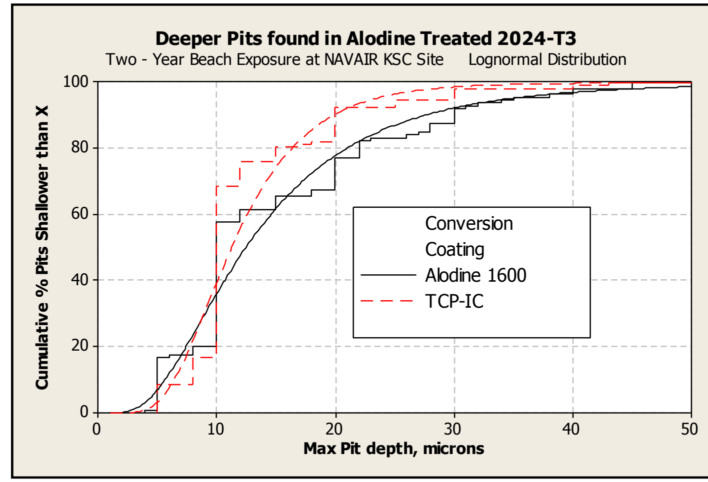
Source: Greg Swain, MSU, **Structure, Function and Stability of Trichrome Process Coatings Formed on Aluminum Alloys, unpublished**

Source: Jerry Frankel, OSU 2010 SERDP Interim Report

Failure Mechanisms for TCP Films

- Outdoor exposure test of TCP coatings has produced favorable results
- Serial grinding / metallographic pit measurements at UTRC of NAVAIR –supplied, 2-year beach samples show shallower, less numerous pits in TCP-treated 2024-T3 Al than in chromate-treated 2024-T3 Al
- UTRC Contact mode AFM images of these samples indicate potential local failure of chromate film associated with pitting after 2 years
- Visual inspection of salt spray failures indicates that pits nucleate near intermetallic particles on TCP-treated Al

Source: UTRC, P&W Green Engine Program

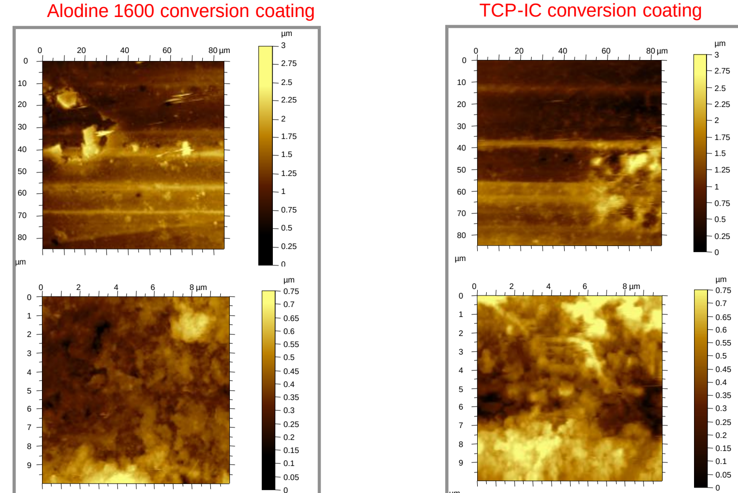


Beach Corroded Samples: 2024 Al Alloy

Contact AFM Imaging of 'As Received' Samples

Alodine 1600 conversion coating

TCP-IC conversion coating



TCP / 2024-T3 "Infant Mortality" failure after 48 hrs neutral salt spray

Source: Martin Piech, 2010 PSD Capability Project

How To Succeed with TCP…

Part 1: Pretreatment Effects on TCP Inhibition

Dr. Michael Kryzman, UTRC Materials Chemistry
Dr. Mark Jaworowski, UTRC Advanced Materials

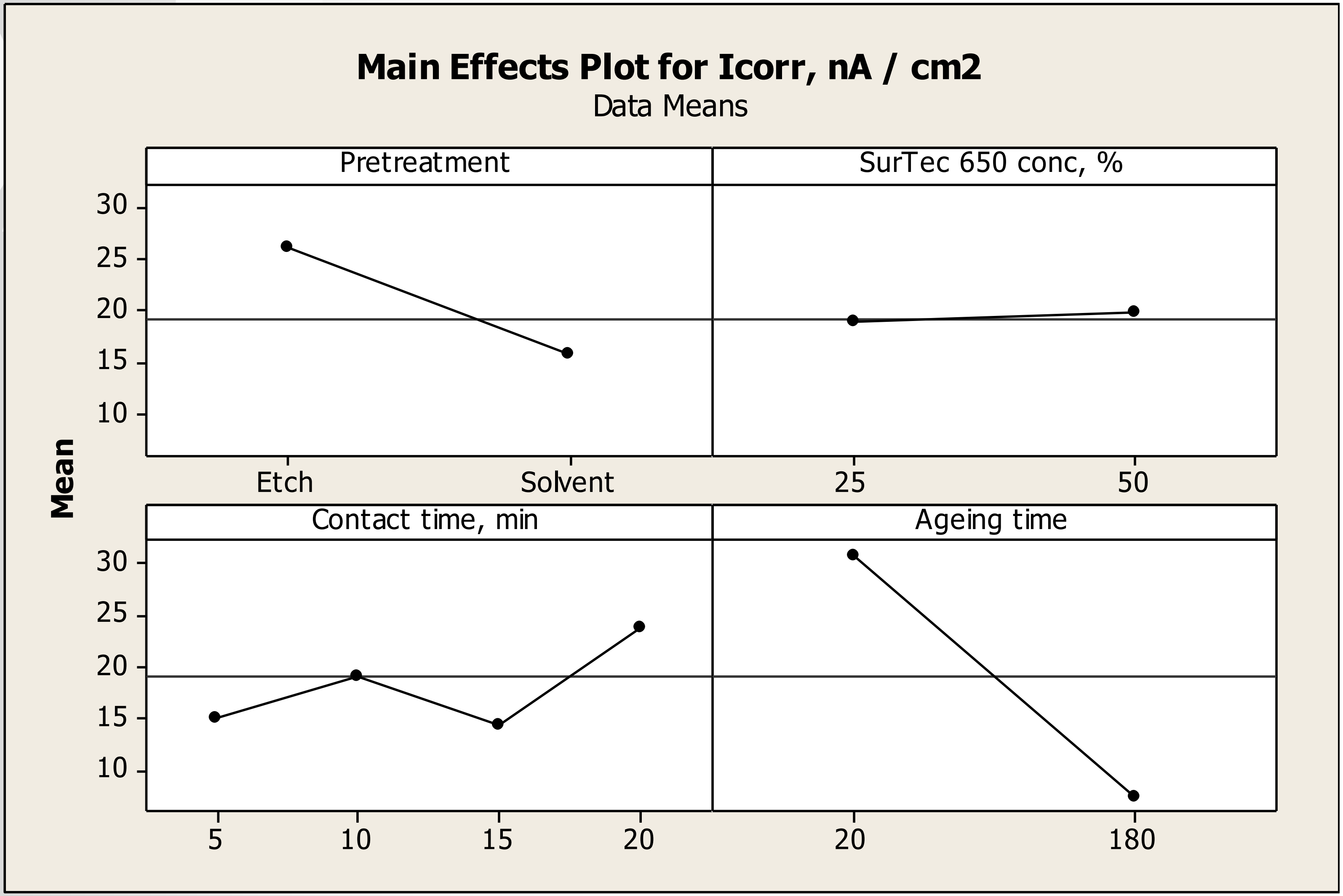
Initial Experimental Design

Two-level fractional factorial plan for four parameters

Test runs	Parameters			
	Pretreatment	SurTec 650 concentration in DI water, %	SurTec 650 treatment time, min	Ageing time, hrs
1	HNO_3	50	20	20
2	HNO_3	50	10	180
3	TCE	25	10	180
4	TCE	50	20	180
5	HNO_3	25	10	20
6	TCE	50	10	20
7	HNO_3	25	20	180
8	TCE	25	20	20

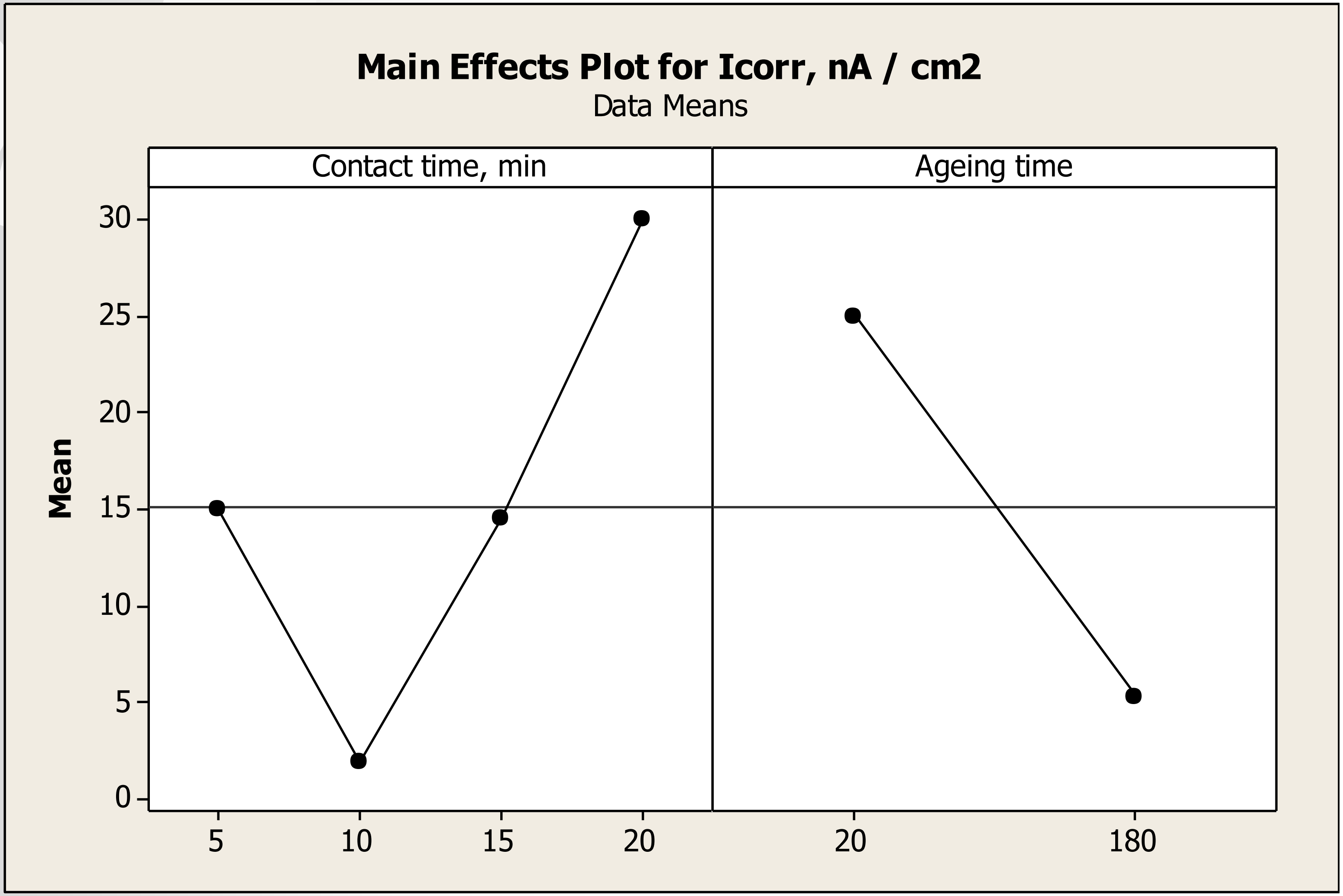
Main Effects from Initial Experiment and Supplement #1

Mild pretreatment, sample ageing improve corrosion resistance



Solvent cleaned / 25% Concentration data

An optimal contact time is indicated for the TCP coating process



Path to robust anticorrosion conversion coatings for 2000-series Al

TCP coatings form, protect and fail through interactions with intermetallic particles on the surface of 2024-T3 Al

Existing performance is encouraging but not robust enough

The key to the necessary further improvements is likely to reside in improved processing based on knowledge of process / structure / inhibition relationships

<u>To obtain best results with commercially available systems:</u>

Avoid heavy etch pretreatments

Control contact time to avoid under- and over-processing

Realistically “age” development and validation samples prior to testing

2. Non chromate treatments for surface conductivity preservation

MIL-DTL-81706B defines two classes of conversion coatings for Al alloys:

> 1.2.2 Classes. The materials, which form protective coatings by chemical reaction with aluminum and aluminum alloys, are of the following classes (see 6.2).
>
> Class 1A - For maximum protection against corrosion, painted or unpainted.
>
> Class 3 - For protection against corrosion where low electrical resistance is required.

3.7 Contact electrical resistance properties (class 3 only). When tested in accordance with 4.5.5, the contact electrical resistance of aluminum alloy panels treated with class 3 materials under an applied electrode pressure of 200 pounds per square inch (psi) shall be not greater than 5,000 microhms psi as applied and 10,000 microhms psi after salt spray exposure specified in 4.5.1. Individual readings not greater than 20 percent in excess of the specified maximums shall be acceptable, provided that the average of all readings does not exceed the specified maximum resistance.

Apparatus for contact electrical resistance measurement

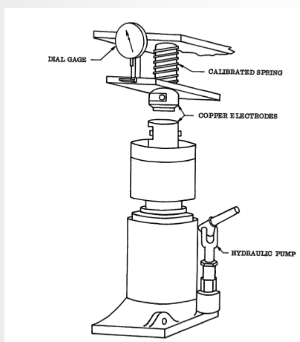
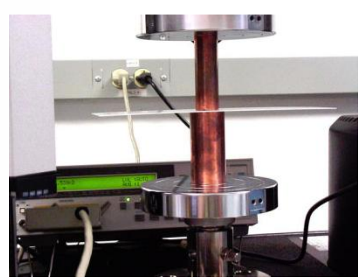


FIGURE 1. Sketch of equipment for measuring electrical resistance of chemical film.



Bridge circuit for contact electrical resistance measurement

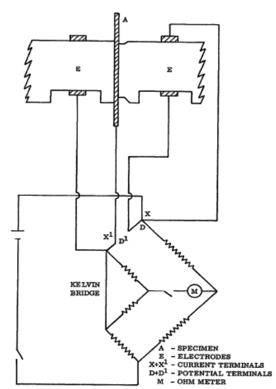


FIGURE 2. Circuit diagram for contact resistance measurements.

Class 3 Coatings are Most Likely Dielectric…

G.E. Pike (Sandia National Lab) November 1981 SNL Internal Report

Surface resistance of Alodine 1200 chromate conversion coatings on 6061 Al were measured using a mercury drop apparatus

Samples were tested at different coating weights, with and without thermal curing, at DC and frequencies up to 10^6 Hertz

In all cases, samples were dielectric (insulators)

Class 3 coatings likely exhibit surface conductivity under mechanical load due to film fracture / metal / metal contact

This effect is likely controlled by film thickness, surface roughness, film strength and ductility of the copper anvils

Better understanding of these effects will assist in validating non-chromate Class 3 coatings

Recommend recording resistance as a function of load in future testing to detect and characterize pressure required for film break-induced conductivity

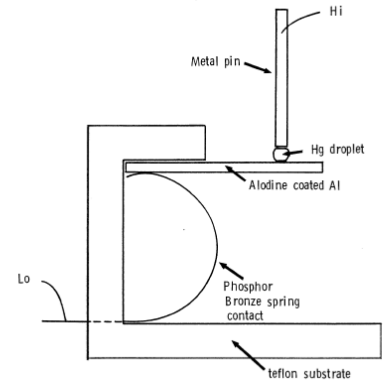


Table I

Sample	Etch (seconds)	Immersion (minutes)	Heat Treatment
A1	15	none	none
W2-A	30	1	none
W2B	30	1	68-74°C, 16 hours
W2C	30	1	68-74°C, 16 hrs 119-127°C, 7 hrs
Z2-A	15	3	none

Table II

Sample	V_{dc} (volts)	Frequency (Hz)	Capacitance (pF)	Resistance (Ω)
A1		0	-	3 ± 1
W2-A-1	1	0	-	6×10^{7}
W2-A-2	1	0	-	5×10^{9}
W2-A-3	0	10^3	79.8	3.3×10^{6}
		10^4	27.0	9.9×10^{5}
		10^5	17.5	3.7×10^{5}
		10^6	14.1	8.9×10^{4}
W2-B	1	0	-	$8 \pm 2\times10^{11}$
W2-C	1	0	-	7×10^{12}
	10	0	-	7×10^{11}
	25	0	-	2×10^{11}
	50	0	-	breakdown
	25	0	-	1.4×10^{9}
Z2-A	1	0	-	3×10^{10}
	0	10^3	1.42	1.3×10^{9}
		10^4	1.31	3.2×10^{8}
		10^5	1.27	7.7×10^{7}
		10^6	1.24	2.5×10^{7}

Scientific Understanding of Nonchromate Inhibitors Function

Task 5 of SERDP Project "Scientific Understanding of Nonchromate Inhibitors Function" with OSU Fontana Corrosion Center (Lead) and Michigan State University

Project Team – Main Performers

- **Dr. Gerald S. Frankel and Dr. Rudolph G. Buchheit**
  Fontana Corrosion Center, The Ohio State University
  Specialists in corrosion

- **Dr. Greg Swain**
  Dept of Chemistry, Michigan State University
  Specialist in electrochemistry/surface analysis

- **Dr. Mark Jaworowski**
  United Technologies Research Center
  Specialist in surface treatments
- **Dr. Weina Li,** UTRC Materials Chemistry
- **Dr. Xiaomei Yu**, UTRC Advanced Materials

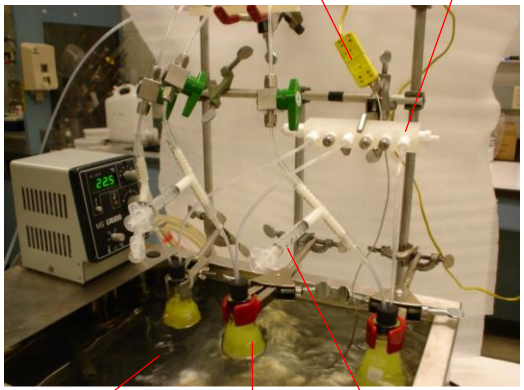
Inhibitor Activation and Transport in Primers

Analysis of anticorrosion primers 2008

Material Characterized	Form	Active corrosion inhibitor
Bond Primer A	Adhesive bond primer, cured film	Calcium silicate, zinc phosphate
Paint Primer B	Paint primer, liquid resin	Praseodymium hydroxide
Paint Primer C	Paint primer, liquid resin	Praseodymium hydroxide
Paint Primer E	Paint primer, liquid resin	Praseodymium hydroxide
Paint Primer F	Paint primer, liquid resin	Calcium and magnesium silicate
Paint Primer G	Paint primer, liquid resin	Zinc oxide, aluminum phosphate
Paint Primer H	Paint primer, liquid resin	Magnesium hydroxide
EcoTuff™	Inhibitive pigment	Cerous citrate, zinc molybdate

Chemical Solubility Tests 2008-2009

Thermocouple manifold



Water bath for temperature control

Test flask

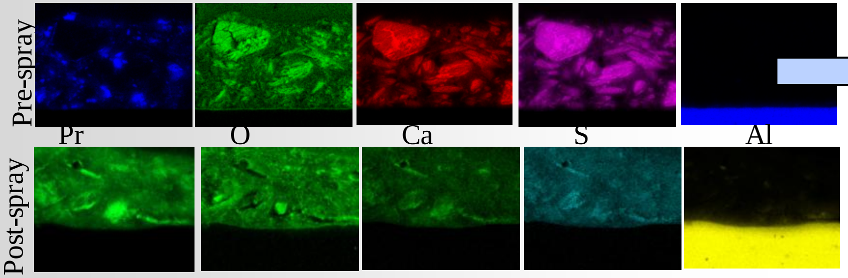
Syringe for in-situ sampling

Analysis of aged primer films 2009

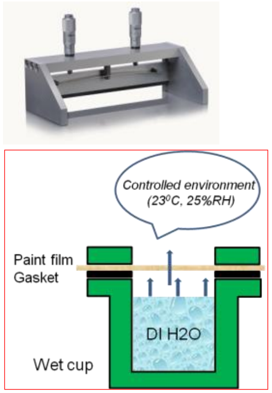
2,000-Hour Salt Spray Exposure Effect on $Pr(OH)_3$ / $CaSO_4$ Pigment

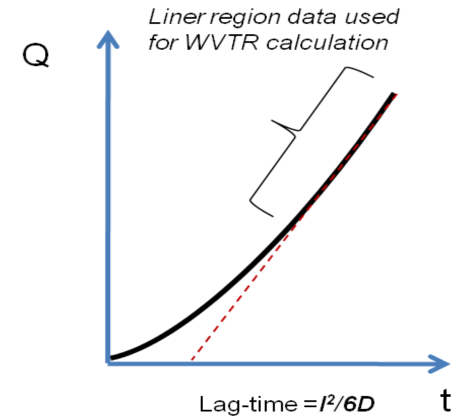
Primer sample on 20424- T3 Al with Alodine 600 chromate conversion coating

EDX Maps



Measurement of water / inhibitor transport 2010



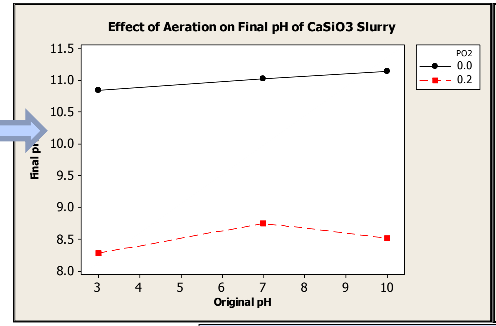


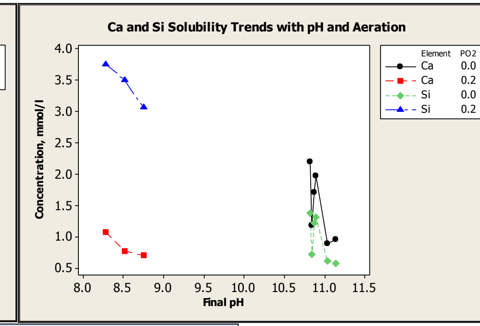
Chemical reactions controlling non-chromate inhibitor activation

1. Reactions with atmospheric CO_2 regulate solubility and ageing behavior of anticorrosion pigments based on silicate inhibitors

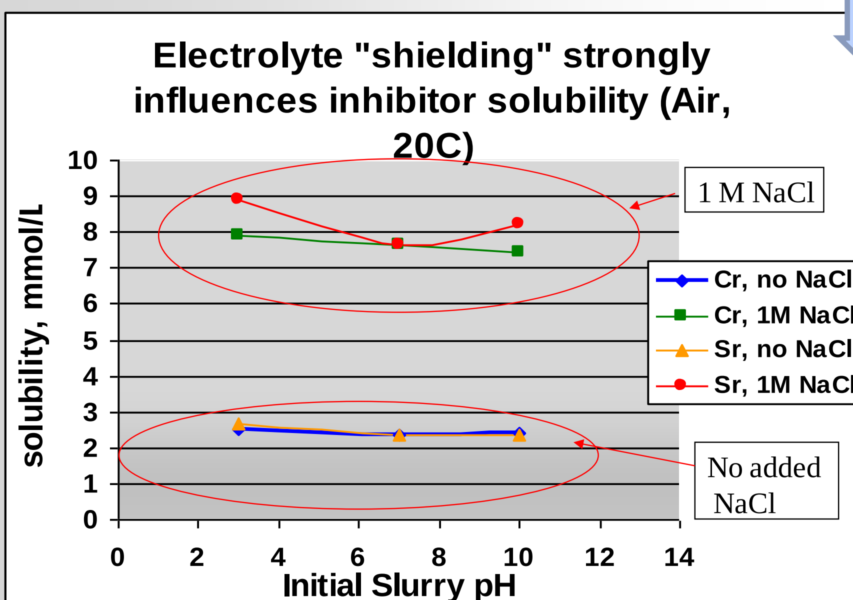
2. Inter-pigment chemical reactions to activate and transport corrosion inhibitive praseodymium ions

3. Electrolyte effects profoundly enhance all pigment solubilities. Corrosive environments increase pigment release rates. Cyclic condensation testing needed to accurately reflect field weathering behavior.





$$CaSiO_3 \longrightarrow Ca^{2+} + SiO_3^{2-} \quad (1)$$
$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3\downarrow \quad (2)$$
$$Ca^{2+} + 2OH^- \longrightarrow Ca(OH)_2\downarrow \quad (3)$$



$Pr(OH)_3$ Solubility Measurements

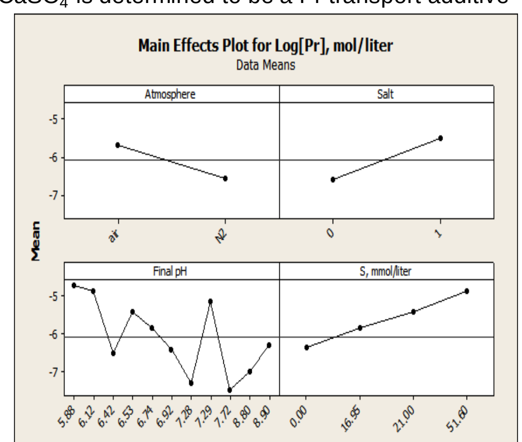
Atmosphere has strong effect, due to CO_2 acidification

Strong "electrolyte shielding" solubility promotion effect

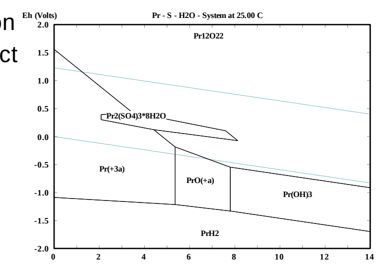
Lower pH benefits higher solubility

Sulfate addition forms stable Pr – S complexes

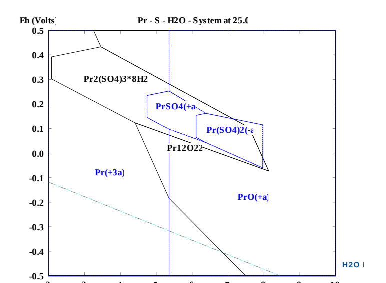
$CaSO_4$ is determined to be a Pr transport additive



Thermodynamic Framework



Pr-S-$H_2$0 Stability Diagram



Expanded scale, with ion predominan

Mapping of Inhibitor Fields in Primers

1. Weathering trends identified Pr-bearing primer samples exposed to 2000 hour salt spray test
   - Disappearance of original $CaSO_4$ pigment particles
   - Inhibitive Pr becomes distributed through the primer matrix

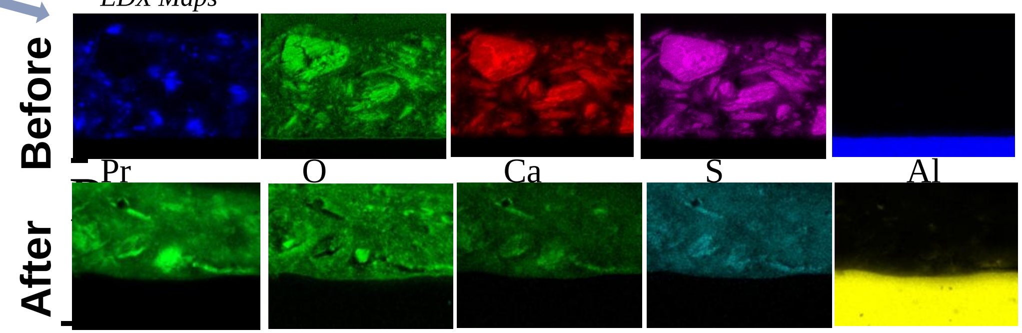
2. Statistical analysis of element mapping data reveals additional trends (local associations of Pr with Ca, S).
   - Likely a good coating for acidic, SO_2-rich environments
   - May fail when $CaSO_4$ is depleted

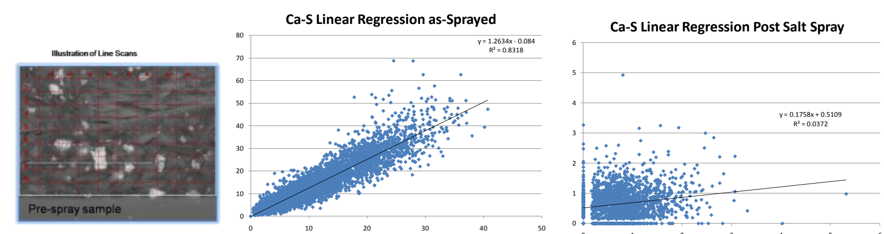
3. Weathering analysis of silicate-bearing primer shows silicate distribution into primer matrix
   - Calcium loss (as $CaCl_2$?) may be life-limiting

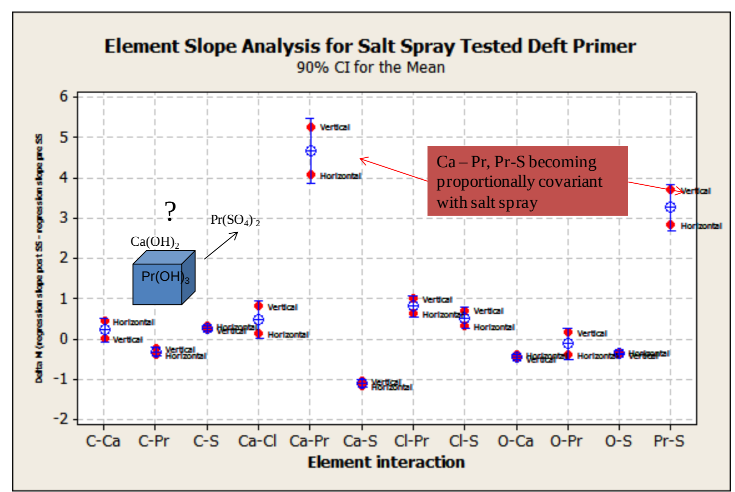
2,000-Hour Salt Spray Exposure Effect on Pr-inhibited Primer

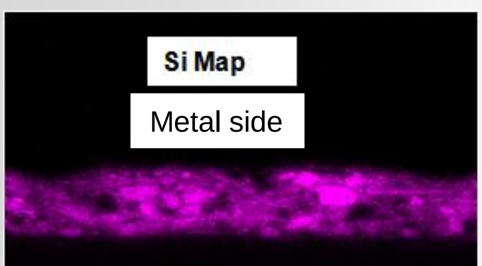
Primer sample on 2024-T3 Al with Alodine 600 chromate conversion coating

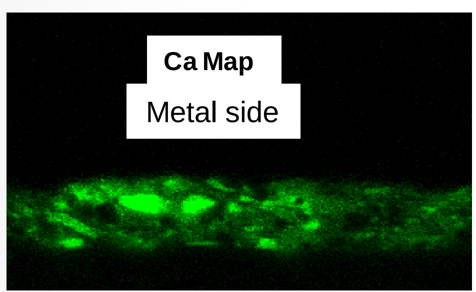
EDX Maps







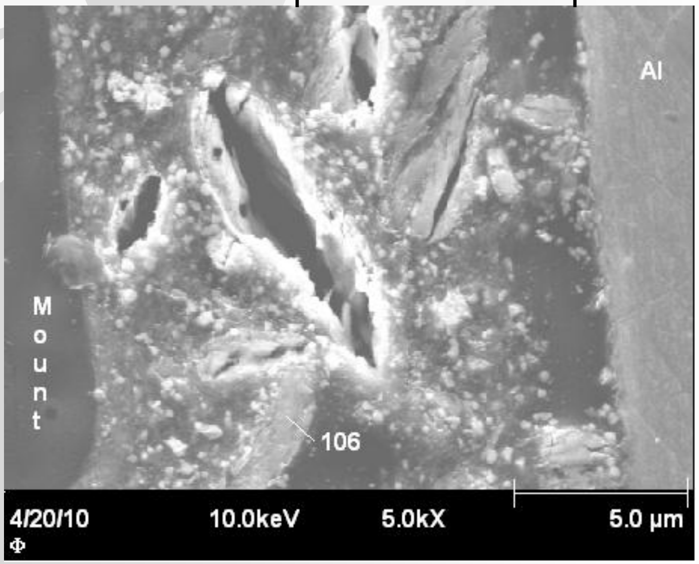




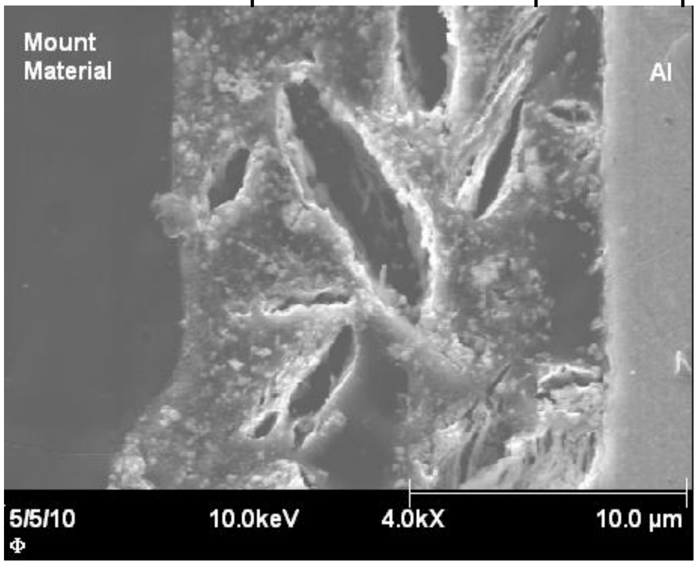
Localized Ca Enrichment in Pr-base Primer Post Salt Spray

Cracks develop in Ca-rich phase under vacuum exposure

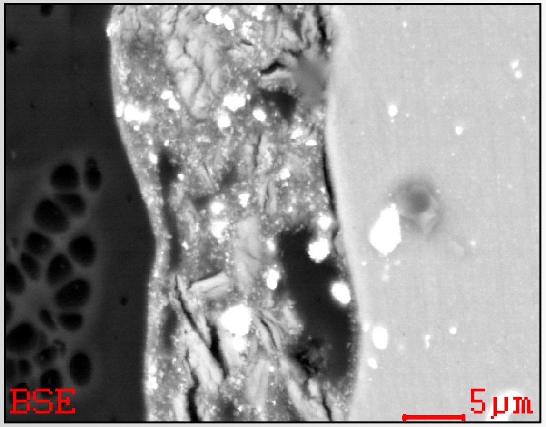
1st Vacuum exposure – 100 A sputter depth



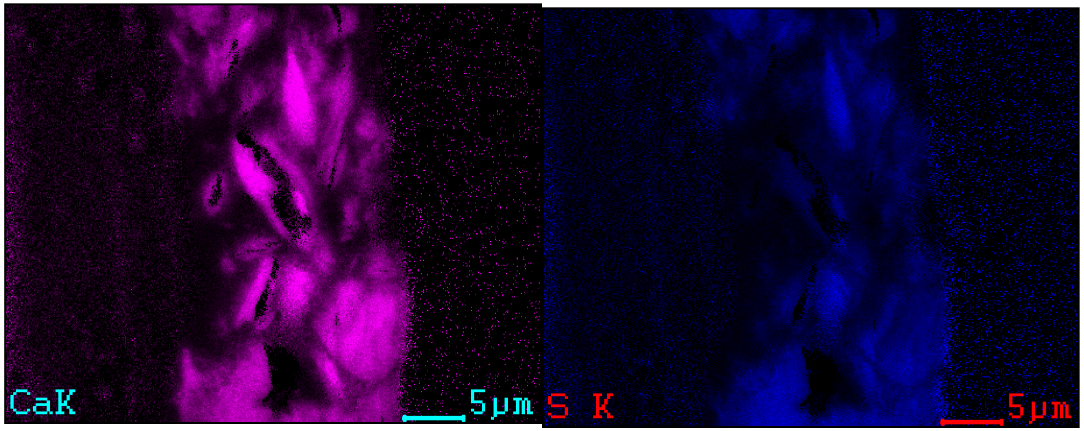
2nd Vacuum exposure – 200 A Sputter depth



Cracks in non-sputtered region



Cracked phase is rich in Ca



2011-2014 SERDP Project Proposal
“Understanding Corrosion Protection Requirements for Adhesive Bond Primers”

Rationale: Currently-available non-chromate bond primers do not provide robust corrosion inhibition to Al alloys in standard tests. Contribution of corrosion to bond line failures is not understood. Requirements for corrosion inhibition are now based on the capabilities of strontium chromate anticorrosion pigment.

Objectives include:

- Understanding the role of corrosion in adhesive bond joint decay
- Design of tests and samples relevant to bonded structures
- Testing of chromate and nonchromate adhesive bond primer systems
- Creation of corrosion risk assessment methodology for adhesively-bonded structures

Project selected by SERDP for Funding 2011-2014

Hexavalent chromium exposure threat in manufacture and repair

Performers

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Summary

1. Hexavalent Cr compound elimination is a challenge to the aerospace industry
2. Significant progress is being made implementation of safer alternatives for painting and anodizing
3. Significant technical challenges remain in certain areas that may require advances in materials, process and characterization techniques:
   a) Robust conversion coatings for corrosion protection of high strength Al alloys
      - Process improvements needed
   b) Stable surface conductivity with chromate free Al treatments
      - Anvil test technique may not reflect product requirements
   c) Chromate free adhesive bond primer systems
      - New materials and pretreatment processes likely to be needed to replace chromated bond primers for Al

Questions ?